G -type antiferromagnetic order in the metallic oxide LaC u3 C r4 O12

Supplementary Material for "G-type antiferromagnetic order in metallic oxide $LaCu_3Cr_4O_{12}$"

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Here we provide the results of the Rietveld analysis of the neutron powder diffraction (NPD) data of $LaCu_3Cr_4O_{12}$, details of the bond valence sum calculations, and the details of the calculated density of states (DOSs) of the lowest energy model.

The result of the fitting for the NPD data at 300 K is shown in Fig. S1. The refined structural parameters at 300 K are summarized in Table S-I, and the selected bond distances and bond angles at 300, 250, 200 and 5 K are summarized in Table S-II. The refined magnetic moments of the B-site Cr spins obtained with the temperature dependent NPD data are plotted in Fig. S2.

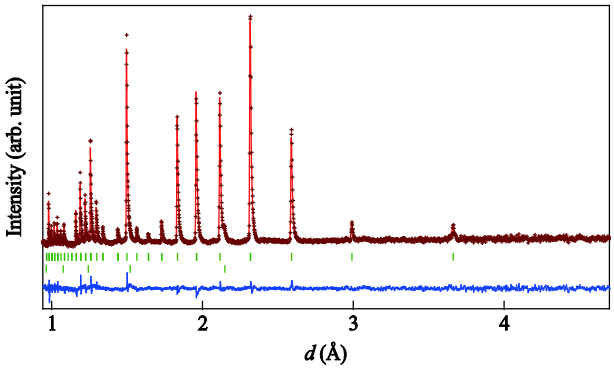

FIG. S1. Rietveld plot of the neutron powder diffraction pattern of $LaCu_3Cr_4O_{12}$ at 300 K. The observed (+) calculated (solid line) patterns are shown along with the difference between them (bottom). The ticks indicate the allowed Bragg reflections for $LaCu_3Cr_4O_{12}$ (above) and the vanadium container (below).

TABLE S-I. Results of the Rietveld refinement of the neutron powder diffraction data for $LaCu_3Cr_4O_{12}$ at 300 K. The Wyckoff positions in space group *Im*−3, coordinates, isotropic atomic displacement parameter B_{iso}, site occupancy, and lattice parameter are listed together with the reliability factors.

Atom	Wyckoff pos.	*x*	*y*	*z*	B_{iso} (Å^2)	Occ.
La	2*a*	0	0	0	1.5(1)	1
Cu	6*b*	0	½	½	0.62(9)	1
Cr	8*c*	¼	¼	¼	0.5(1)	1
O	24*g*	0	0.1786(2)	0.3055(2)	0.92(9)	1
a = 7.3198(2) Å						
R_{wp} = 2.50 %, R_B = 4.08 %						

TABLE S-II. Selected bond distances and bond angles of $LaCu_3Cr_4O_{12}$ at 300, 250, 200, and 5 K.

Temperature	300 K	250 K	200 K	5 K
Bond distances /Å				
La–O (×12)	2.590(2)	2.585(2)	2.589(1)	2.590(1)
Cu–O (×4)	1.933(2)	1.946(2)	1.9324(8)	1.917(1)
Cu–O (×4)	2.7498(8)	2.750(2)	2.750(1)	2.7506(5)
Cu–O (×4)	3.246(1)	3.234(2)	3.2448(9)	3.2557(7)
Cr–O (×6)	1.9460(5)	1.9422(7)	1.9454(4)	1.9484(9)
Bond angles /degree				
Cr–O–Cr	140.23(8)	140.89(3)	140.23(2)	139.47(6)
O–Cr–O	90.01(7)/89.99(7)	90.3(2)/89.7(2)	90.03(5)/89.97(6)	90.10(5)/89.90(5)
Cr–O–Cu	109.6(1)	109.24(8)	109.59(4)	109.97(5)

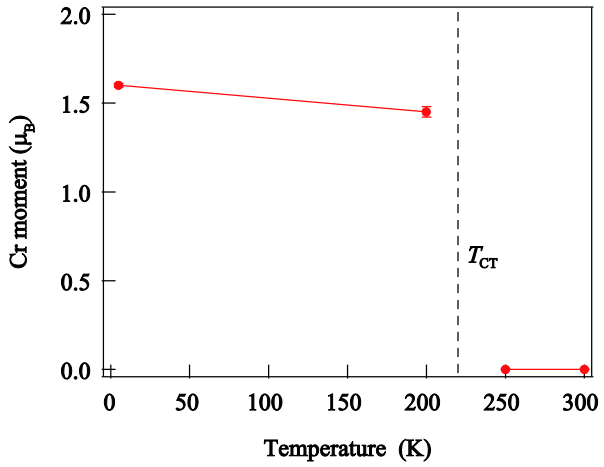

FIG. S2. Temperature dependence of the refined magnetic moment at Cr site obtained from the Rietveld analysis of the neutron powder diffraction data. Charge transfer transition temperature is shown by a broken line.

The results of the NPD structure analysis with the accurate bond distances r_i from the cation site to the coordinating oxygens enable the formal charges of the cations to be estimated using the bond valence sum method [1]. Bond valence sum (V_N) is given by the formula $V_N = \Sigma_i \exp[(r_N - r_i)/0.37]$, where r_N is the bond valence parameter for the metal in an assumed oxidation state N. The charges of the mixed valent Cu and Cr were estimated by interpolation between V_N values obtained for Cu^{2+}/Cu^{3+} and Cr^{3+}/Cr^{4+}, using the formula $V_N = [L(V_H - V_L) - (H - L)V_L]/[(V_H - V_L) - (H - L)]$, where H and L are the higher and lower formal oxidation states [2]. As the r_4 for 6-fold coordinated Cr^{4+}–O^{2-} bond in ref. 1 is not reliable, it was calculated using the previously reported bond distances of $SrCrO_3$ [3], $CaCrO_3$ [4] and CrO_2 [5,6]. r_4 was calculated for each reported structure assuming $V_4 = 4.00$ for Cr [7], and the averaged value of 1.756 was used in the present study. Bond valence sums of Cu and Cr were summed over 12 and 6 bonds, respectively. The interpolated charges were normalized to the total of +21 for the formal sum of the Cu and Cr charges per formula unit. The resulting charges are $LaCu^{2.47+}{}_3Cr^{3.39+}{}_4O_{12}$ at 300 K (corresponding to $\delta = 0.47$) and $LaCu^{2.59+}{}_3Cr^{3.31+}{}_4O_{12}$ ($\gamma = 0.41$) at 5 K. The estimated intersite charge transfer is 0.12e per Cu ion. The obtained results are consistent with the previously reported results obtained from the synchrotron X-ray diffraction data [7].

We also provide the results of the *ab initio* calculations. Total energy of a spin polarized model with nonmagnetic Cu and G-type AFM Cr spins was compared to those with a paramagnetic case with nonmagnetic Cu and Cr ions, and a ferrimagnetic case with antiferromagnetically coupled FM sublattices of Cu and Cr spins. Electron correlations are taken into account in the calculations. The results are summarized in Table S-III.

TABLE S-III. Total energy differences in spin polarized models.

(1) Standard calculation without U_{eff}

Model	nonmagnetic Cu & G-type AFM Cr	Paramagnetic: PM Cu & PM Cr	Ferrimagnetic: FM Cu & FM Cr	Ferromagnetic: FM Cu & FM Cr
Energy difference (eV)	-	+2.07	+0.16	converged to a ferrimagnetic model

(2) Calculation with U_{eff} = 2 eV for *B*-site Cr

Model	nonmagnetic Cu & G-type AFM Cr	Paramagnetic: PM Cu & PM Cr	Ferrimagnetic: FM Cu & FM Cr	Ferromagnetic: FM Cu & FM Cr
Energy difference (eV)	-	+4.80	+0.41	converged to a ferrimagnetic model

(3) Calculation with U_{eff} = 2 eV for *A'*-site Cu and U_{eff} = 2 eV for *B*-site Cr

Model	nonmagnetic Cu & G-type AFM Cr	Paramagnetic: PM Cu & PM Cr	Ferrimagnetic: FM Cu & FM Cr	Ferromagnetic: FM Cu & FM Cr
Energy difference (eV)	-	+4.83	+0.12	converged to a ferrimagnetic model

(4) Calculation with U_{eff} = 4 eV for *B*-site Cr

Model	nonmagnetic Cu & G-type AFM Cr	Paramagnetic: PM Cu & PM Cr	Ferrimagnetic: FM Cu & FM Cr	Ferromagnetic: FM Cu & FM Cr
Energy difference (eV)	-	+8.15	+0.55	converged to a ferrimagnetic model

Even when electron correlations were taken into account in the calculations, the spin polarized model with nonmagnetic Cu and G-type AFM Cr spins, which was confirmed by NPD magnetic structure analysis, was found to give the lowest total energy. Therefore, the discussion in the present study was based on the result with (1) standard calculation without U_{eff}.

The calculated total and partial DOSs of the experimentally obtained spin structure are shown in Fig. S3. The bands approaching the Fermi level (E_F) at the R point have rather linear *k*-dependences like a Dirac cone along the Γ–R direction, as shown in Fig. S4, although those above and below E_F rapidly bend back away from each other in the very vicinity of the R point. Magnetoresistance as reported for some Dirac electron systems was not observed for the present $LaCu_3Cr_4O_{12}$.

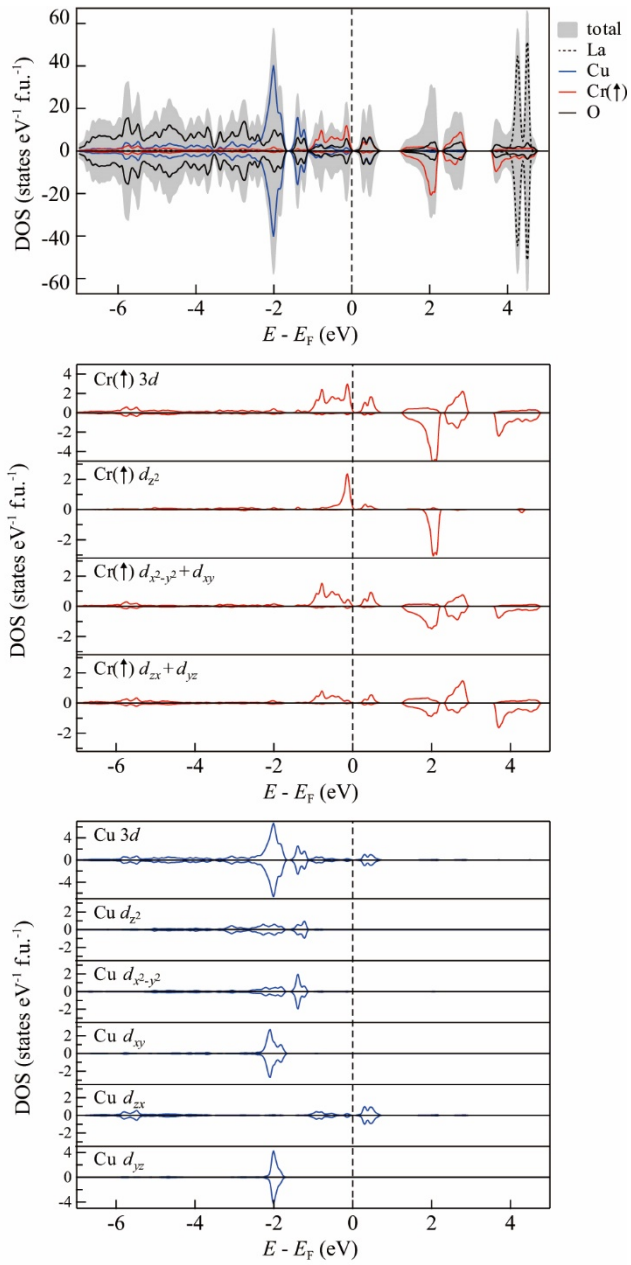

FIG. S3. Calculated total and partial DOSs for $LaCu_3Cr_4O_{12}$. E_F is the Fermi energy.

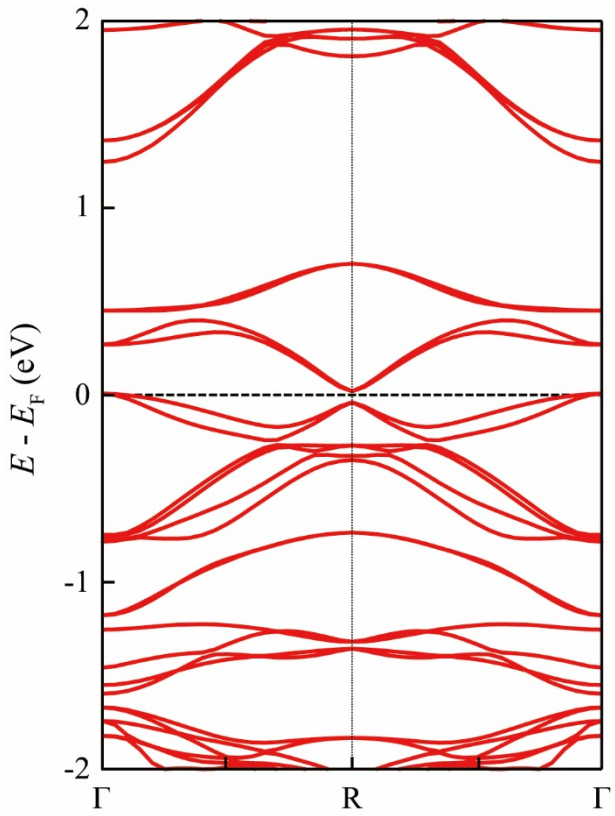

FIG. S4. The band structure along the Γ–R direction.

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